

CFC's in the Unsaturated Zone and in Shallow Ground Water at Mirror Lake, New Hampshire

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ABSTRACT

At the U.S. Geological Survey's fractured-rock hydrology research site at Mirror Lake, N.H., concentrations of chlorofluorocarbons (CFC's) and other chemical constituents in ground water were measured to help identify large-scale flow and transport properties of the crystalline bedrock. The use of CFC's as environmental tracers in ground water is based on the assumption that CFC concentrations in recharge are in equilibrium with atmospheric levels. Results of a 3-year field study to identify the input source function for CFC's in ground-water recharge indicate that use of CFC's as an environmental tracer at this site, and presumably at other forested, humid sites underlain by glacial deposits, may be significantly complicated by anaerobic degradation reactions in shallow ground water. CFC concentrations near the water table are depleted where dissolved oxygen levels are low. CFC-11 and CFC-113 are absent under anaerobic conditions; CFC-12 is as low as one-third of modern concentrations. Methanogenic and sulfate-reduction conditions have been identified by use of hydrogen-gas measurements, and methane has been detected in several anaerobic samples. One area of active degradation appears to be associated with streamflow loss to ground water. Soil-gas concentrations are generally close to atmospheric levels, although limited spatial correlation is observed between depleted concentrations of CFC-11 and CFC-113 in soil gas and water-table samples.

CFC'S AS ENVIRONMENTAL TRACERS

Chlorofluorocarbons (CFC's; also called Freon, chlorofluoromethane) have emerged as useful age-dating tracers for young ground water (Plummer and others, 1993). The atmospheric source for CFC's is relatively well known and is almost linear in time, and the CFC concentration of fresh water in equilibrium with the atmosphere is well described as a function of temperature alone. CFC-12, CFC-11, and CFC-113 are man-made volatile organic compounds that are widely used as refrigerants and components of many manufactured goods. The atmospheric concentration of CFC's has been increasing since their creation in the 1940's, although concentrations have very recently begun to level off, and slightly decrease for CFC-11, due to production reductions and losses from the atmosphere.

Assuming that recharging ground water is in CFC equilibrium with the atmosphere, a measured CFC concentration in water can be converted to a corresponding atmospheric concentration, which in turn can be used to compute a corresponding date of recharge. The difference between the date of recharge and the

date of sampling is the apparent age of the ground water.

The dating of ground water with the use of CFC's depends, in part, on the assumption that CFC's are inert; once isolated from the atmosphere, the CFC concentration in moving water is constant in time. However, several processes may change CFC concentrations during flow. These processes include mixing and dispersion, exchange with solids, gases, or immobile waters, and degradation by biotic or abiotic reactions (Busenberg and Plummer, 1992). It is known that CFC's, particularly CFC-11 and CFC-113, are degraded under anaerobic conditions in ground water (Semprini and others, 1990; Terauds and others, 1993; Oster and others, 1996; Plummer and others, 1998). In oxygenated waters, however, CFC's appear to be virtually inert. Furthermore, the gradual increase in atmospheric concentrations over time means that CFC concentrations are less affected by mixing and dispersion than are tracers with highly variable sources, such as tritium (Plummer and others, 1993). Exchange processes may be important for CFC's, especially in highly heterogeneous formations such as fractured rock (Shapiro, 1996; Wood and others, 1996). Sorption of CFC's to most natural aquifer materials is believed to be

insignificant. Despite these beneficial factors, CFC concentrations in ground water are not always easy to interpret. The U.S. Geological Survey (USGS) Mirror Lake, N.H., research site is one location where CFC's have not been as useful as hoped in characterizing large-scale transport properties (Busenberg and Plummer, 1996; Shapiro and others, 1996).

MIRROR LAKE FIELD SITE

The USGS is investigating multi-scale flow and transport in a glaciated fractured-rock setting at the Mirror Lake, N.H., site (Winter, 1984; Shapiro and Hsieh, 1996; Hsieh and others, 1993; several other papers in these proceedings). This site is part of the Hubbard Brook Experimental Forest, administered by the U.S. Forest Service (USFS). Ground water from the fractured bedrock and from the overlying glacially deposited formations has been analyzed for numerous environmental tracers (Busenberg and Plummer, 1996; Drenkard and others, 1996).

Hydrogeologic Setting

Glacial drift overlies crystalline bedrock at the Mirror Lake site (Winter, 1984). The glacial drift has a highly variable composition ranging from uniform sandy terraces to fine-grained till filled with large boulders (Winter, 1984; Harte, 1992; Harte and Winter, 1995, 1996). The permeability of the glacial drift is generally low (Wilson, 1991; Harte, 1997). Regional-scale flow modeling indicates the transmissivities of the glacial drift and the underlying fractured bedrock are low and of the same order of magnitude (Tiedeman and others, 1997, 1998). Base flow to streams in the Mirror Lake drainage basin is significantly higher than in other parts of the Hubbard Brook drainage basin because of the increased thickness of glacial drift (Winter and others, 1989; Mau and Winter, 1997). Sandy terrace deposits located throughout the watershed may have strong local control on ground-water flow and ground-water/surface-water interaction (Shattuck, 1991; Harte and Winter, 1995, 1996). The climate is humid and long-term average recharge to ground water is on the order of 30 cm/yr (centimeters per year) (Mau and Winter, 1997).

Ground-Water Ages from CFC Data at Mirror Lake

Ground-water ages derived from CFC concentrations in samples from bedrock wells at Mirror Lake do not follow a readily apparent spatial (vertical and horizontal) distribution (Busenberg and Plummer, 1996; Shapiro and others, 1996). In homogeneous formations, ground-water age is expected to increase gradually along flow paths from recharge to discharge locations. In the highly heterogeneous fractured rock at Mirror Lake, however, in which the small-scale hydraulic conductivity varies over at least seven orders of magnitude (Hsieh and Shapiro, 1996), complex patterns may be expected. No general spatial pattern is observed in apparent ages; indeed, some of the youngest apparent ages measured are close to Mirror Lake, which is the primary discharge area for the basin.

Possible geochemical processes that contribute to the complex age spatial pattern at Mirror Lake, and the corresponding CFC concentration pattern, are in situ processes that modify CFC concentrations. These include, but may not be limited to, sorption, exchange, and degradation. Furthermore, seasonal temperature cycles may cause corresponding cycles in CFC concentrations in recharging waters. These cycles may lead to variability in CFC concentrations along a flow path that may be misinterpreted as variable ages.

SCOPE AND OBJECTIVES

The goals of the field study described here are to characterize the concentrations of CFC's in water recharging the saturated zone at Mirror Lake, to identify the processes that control those concentrations, and to describe the source function for CFC's in infiltrating waters that recharge the saturated zone. The field program (1995-97) investigated the following properties and processes: CFC concentrations at or near the water table, and in the unsaturated zone; temperature cycles where CFC air/water equilibrium is occurring; biogeochemical factors that may be related to CFC concentrations; and hydraulic properties of the unsaturated zone. This paper focuses on CFC concentration results. Details of the methods used and other results are discussed in Goode (1998).

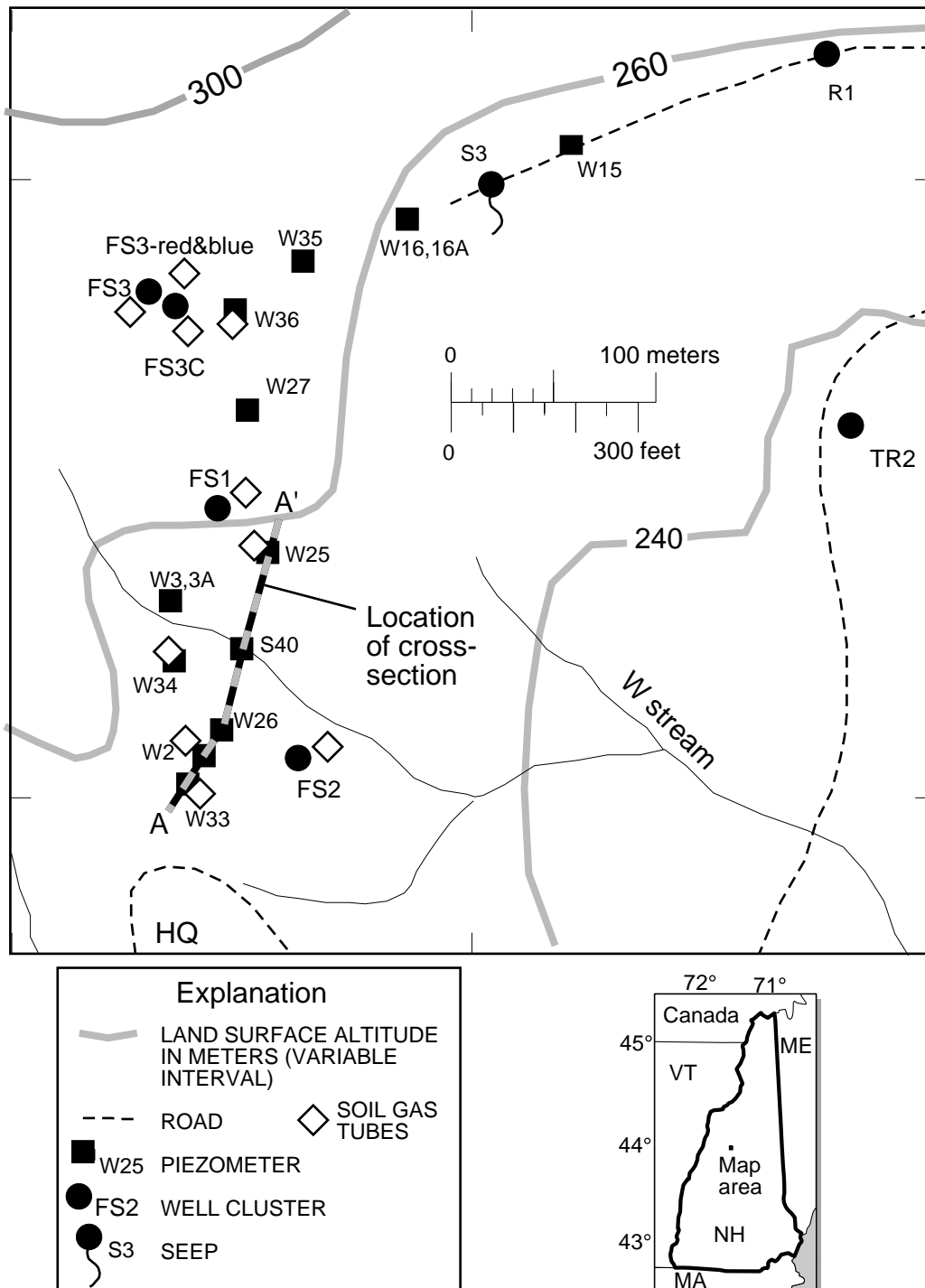


Figure 1. Locations of individual piezometers, well clusters (1-4 piezometers and 1 bedrock well), seep, and soil gas tubes at the Mirror Lake, New Hampshire, research site.

SUMMARY OF METHODS

Some data used in this study were obtained from previous and ongoing research conducted by USFS, Institute of Ecosystems

Studies (IES), USGS, and numerous universities at Mirror Lake and at Hubbard Brook Experiment Forest. Geochemical data, including CFC results from bedrock wells and piezometers, were provided by the USGS national lab and research laboratories. Quality-assurance methods included the collection and

analysis of field blanks and triplicate (or more) water samples. Water-level measurements were also provided by USGS and IES. Barometric pressure data were provided by IES. Precipitation and air-temperature data were provided by USFS, Radnor, Pa. Hydrogen-gas concentrations in water were measured in the field by use of a portable gas chromatograph.

Water samples were collected from 31 shallow piezometers (fig. 1) during the summers of 1995, 1996, and 1997. These piezometers were constructed by USGS over approximately 20 years as part of ground-water/lake interaction studies (Winter, 1984) and of fractured-rock hydrology research (Shapiro and Hsieh, 1996). Piezometers are constructed of either steel or PVC and are almost all screened over 0.6- to 0.9-m (meter) long intervals. This sampling effort focused primarily on piezometers screened near the water table but also included some piezometers screened in the glacial drift beneath the water table. New piezometers constructed for the present study include W16A, W33, W34, W35, and W36. These boreholes were power augered without adding any water during drilling, and the piezometers were constructed of threaded PVC to minimize CFC contamination. Except where the borehole caved in during auger withdrawal, coarse sand was placed in the annulus around the screen, followed by natural backfill, followed by a layer of ground silica flour, and natural backfill to the surface. The purpose of the fine-grained ground silica is to minimize vertical flow within the borehole annulus.

Soil-gas samples were collected during the summers of 1996 and 1997 and in January 1997 from steel soil-gas tubes (fig. 1) installed by hand or power auger or, in one case, by manual drive point. Each soil-gas tube consists of 0.6-cm diameter stainless steel tubing, stainless steel or brass compression fittings, a stainless steel screen, and glass wool. The borehole annulus around the sampling port is filled with coarse sand, followed by natural backfill, followed by ground silica flour, and natural backfill to the surface. Additional details on soil-gas and air sampling methods are given in Goode (1998).

RESULTS

The results of analyses of water samples, including CFC concentrations, and soil-gas CFC concentrations, are summarized below. Other results of this field study, including soil moisture content and temperature monitoring, are described in Goode (1998).

General Chemistry

Field water-quality constituents in water-table piezometers at the Mirror Lake site exhibit significant variability (Goode, 1998). In general, specific conductances are relatively low compared to bedrock wells at the site (Shapiro and others, 1996). The pH ranges from 5 to 11; most values are between 5 and 7. High pH has been associated with cement grout installed at older piezometers (P.T. Harte, USGS, written commun., 1991).

Dissolved oxygen (DO) concentrations are significantly below saturation levels (7-12 mg/L (milligrams per liter)) in many samples from water-table piezometers. In several areas, the water table is apparently anaerobic, or nearly so (fig. 2). This corresponds with the wide-spread observation of low-DO in bedrock wells (Busenberg and Plummer, 1996).

Major ion and dissolved gas concentrations characterize the overall geochemistry of the shallow ground water in the Mirror Lake watershed. The general water type is calcium-bicarbonate-sulfate (Goode, 1998). Concentrations of dissolved nitrogen and argon gas (Goode, 1998) indicate little excess air is present near the water table and the recharge temperature is between 5 and 10°C (degrees centigrade). In contrast to samples from bedrock wells at Mirror Lake (Busenberg and Plummer, 1996), nitrogen and argon concentrations in glacial drift fall approximately along the line corresponding to equilibration with the atmosphere. This suggests the elevated argon and nitrogen in bedrock waters is not due to entrapped or excess air but is caused by some other in situ production. Methane is observed in several samples from water-table piezometers (Goode, 1998). Measurable methane and lack of DO are consistent with methanogenic biodegradation conditions near the water table.

Chlorofluorocarbon Concentrations

Concentrations in Ground Water

About half of the uncontaminated water samples from shallow piezometers contain CFC concentrations near modern (1995-97) atmospheric-equilibrium levels, which are about 950, 450, and 150 pg/kg (picograms per kilogram) for CFC-11, CFC-12, and CFC-113, respectively (at 7 °C). This observation supports use of CFC concentrations to date saturated-zone ground water.

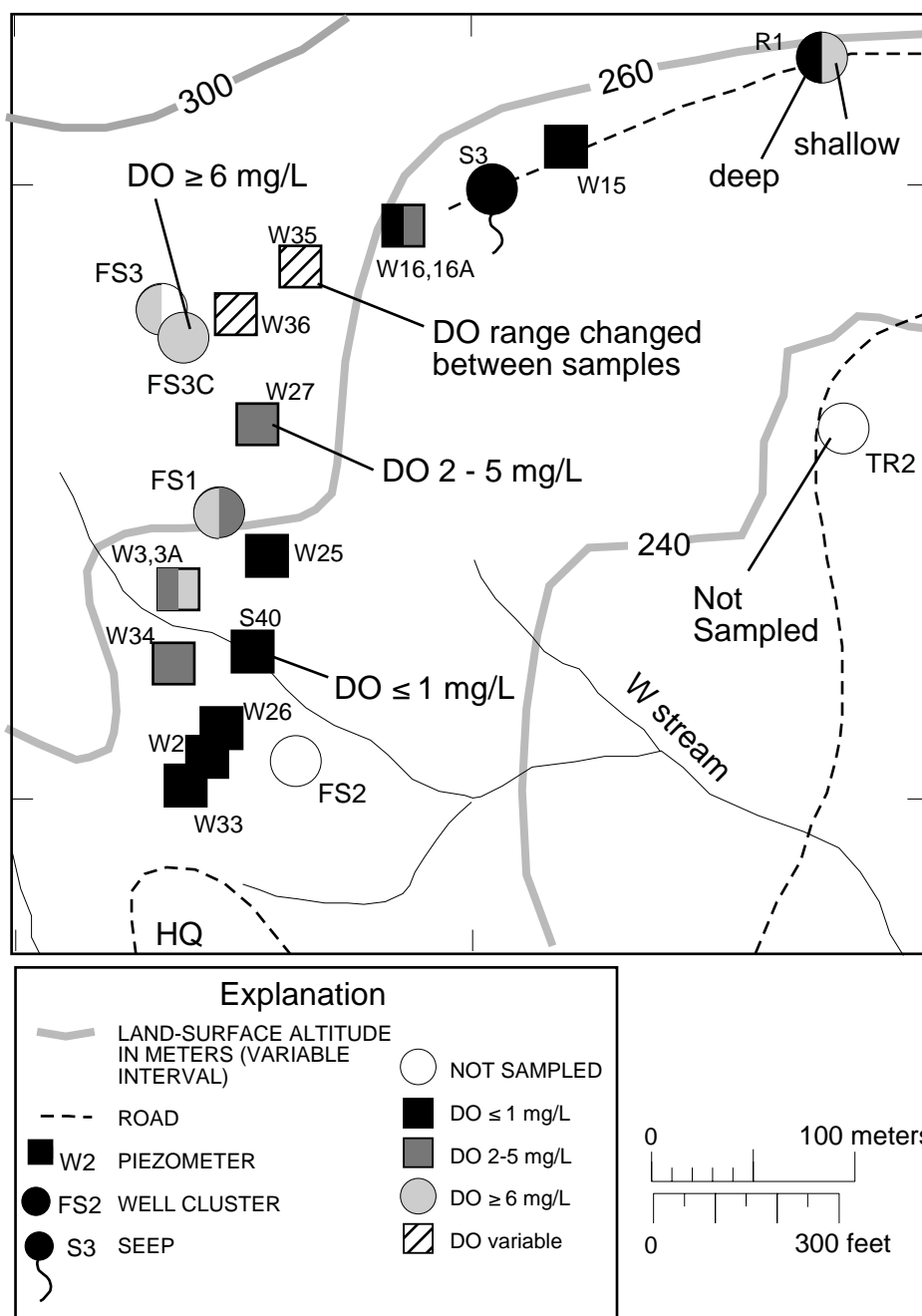


Figure 2. Spatial distribution of dissolved oxygen concentrations in water samples from shallow piezometers at the Mirror Lake, New Hampshire, research site. (Abbreviation: mg/L, milligrams per liter.)

Samples from about one-quarter of the piezometers at Mirror Lake contain CFC concentrations higher than those in equilibrium with the atmosphere. Following Busenberg and Plummer (1992), these samples are designated “contaminated.” In some cases, contamination of samples was so high that the analytical procedures used to concentrate the normal low levels resulted in analytical responses beyond the instrumentation limits. Possible sources of this contamination include sampling equipment

(Busenberg and Plummer, 1996) and well-construction materials, including the sand installed at well screens, grout used to seal the borehole annulus, and PVC adhesives.

About half of the uncontaminated samples collected from water-table piezometers for this study contain CFC concentrations significantly less than those in equilibrium with the modern atmosphere. The observed CFC-12 and CFC-11 concentrations indicate some process is, or several processes are, modifying the

concentrations from atmospheric equilibrium (fig. 3). Water isolated from the atmosphere during the last 50 years should have CFC-12 and CFC-11 concentrations that lie on the atmospheric equilibrium line (shown in fig. 3) if the only process affecting concentrations is advection with moving saturated-zone ground water. The fact that most samples fall below this line indicates more CFC-11 has been removed relative to CFC-12.

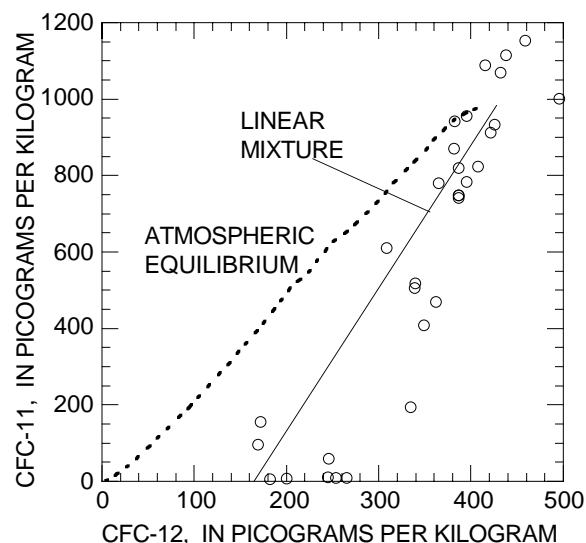


Figure 3. Concentrations of CFC-11 and CFC-12 in water samples from water-table piezometers at the Mirror Lake, New Hampshire, research site. The dashed line shows the concentrations in water in equilibrium with the atmosphere during the last 50 years (at 7 °C). The solid line is a suggested linear mixing line.

A preliminary review of the data indicates that CFC concentrations are correlated with DO. CFC-12 concentrations range from about 160 pg/kg to about 2,300 pg/kg. For uncontaminated samples, CFC-12 concentrations are correlated with DO (fig. 4). Samples containing zero or very small amounts of oxygen have CFC-12 concentrations about 1/3 of the concentration of water in equilibrium with modern air. High oxygen concentrations correspond to CFC-12 concentrations near modern levels.

Concentrations of CFC-11 range from zero to 88,000 pg/kg. Some samples were so highly contaminated with CFC-11 that quantification of the concentrations was not analytically possible. For uncontaminated samples, CFC-11 concentrations are strongly correlated with DO (fig. 4). Samples containing zero or very small amounts of oxygen also

contain zero or very small amounts of CFC-11. High oxygen concentrations correspond to CFC-11 concentrations near modern levels. Taken at face value, these CFC-11 concentrations correspond to ages of 0 years, for the high concentrations, to ages of more than 45 years, for the zero-CFC-11 waters.

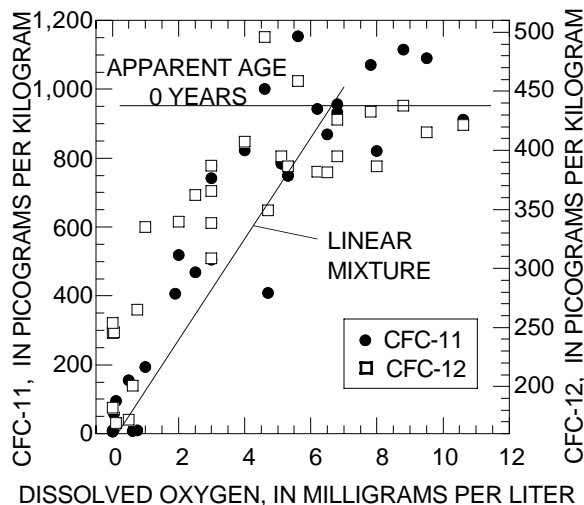


Figure 4. Concentrations of CFC-11, CFC-12, and dissolved oxygen in water samples from water-table piezometers at the Mirror Lake, New Hampshire, research site. The horizontal line corresponds to CFC-11 and CFC-12 concentrations in water equilibrated with the atmosphere at the time of sampling. The solid line is a suggested linear mixing line.

Concentrations of CFC-113 range from zero to 240 pg/kg (Goode, 1998). Some samples were so highly contaminated with CFC-113 that quantification of the concentrations was not analytically possible. For uncontaminated samples, CFC-113 concentrations are strongly correlated with DO, similar to CFC-11 results. Samples containing zero or very small amounts of oxygen also contain zero or very small amounts of CFC-113. High oxygen concentrations correspond to CFC-113 concentrations near modern levels. The scatter in CFC-113 concentrations in high-DO samples is larger than the scatter for either CFC-12 or CFC-11 (Goode, 1998).

The similarity between the correlations of CFC-11 and CFC-12 to DO is shown in fig. 4. The only major difference is that the lowest CFC-12 concentrations correspond to about one-third of modern levels, whereas the lowest CFC-11 concentrations are zero. The correlation between CFC-113 and DO is virtually the same as the CFC-11 pattern but

with more scatter at the upper concentration levels.

The hypothetical mixing line of figs. 3 and 4 corresponds to concentrations of CFC-11 and CFC-12, and dissolved oxygen, in a volumetric mixture of two end-member waters: (a) anaerobic water containing no CFC-11 and 160 pg/kg CFC-12, and (b) water containing 7 mg/L DO, 950 pg/kg CFC-11, and 430 pg/kg CFC-12. Without this mixing, the apparent degradation of CFC's in the presence of 1 to 4 mg/L of dissolved oxygen is difficult to explain because it is assumed that degradation occurs only under anaerobic conditions. Generally, anaerobic conditions are considered to be prevalent when DO is much less than 1 mg/L.

The relation between CFC-11 and tritium in samples from water-table piezometers is shown in fig. 5. Tritium concentrations generally indicate modern recharge (Plummer and others, 1993) but CFC-11 concentrations suggest ages from zero to over 45 years. Almost all measured tritium concentrations are about 10-15 TU (tritium units). All of these tritium concentrations are significantly below bomb-peak levels dating from the late 50's and early 60's. The concentration of tritium in waters recharged in 1963, accounting for subsequent radioactive decay until 1995, would be more than 150 TU (Busenberg and Plummer, 1996), about an order of magnitude higher than measured concentrations. On the basis of the age-dating assumptions, a sample containing zero CFC-11 was recharged prior to 1945. The concentration of tritium in recharge in 1945, decayed to 1995, would amount to less than 5 TU, and older waters would contain even less tritium. The observed tritium and CFC concentrations suggest these water samples represent modern recharge, but CFC concentrations have been reduced by degradation.

Concentrations in Soil Gas

Concentrations of CFC's in soil gas exhibit much less variability than concentrations in water (Goode, 1998). All CFC-12 soil-gas concentrations are close to 100 percent of modern atmospheric levels (fig. 6). The average CFC-12 soil gas concentration at each sampling location ranges from 0.97 to 1.06 times modern air concentrations. CFC-12 concentrations in local air are close to the global average; individual measurements range from 0.93 to 1.07 times the global average.

CFC-11 concentrations in soil gas vary somewhat more than CFC-12 concentrations and are reduced compared to modern air. The

average CFC-11 soil-gas concentration at each sampling location ranges from 0.81 to 1.13 times modern air concentrations. CFC-11 soil-gas concentrations are low near piezometer W33 (fig. 7), where zero CFC-11 is measured in shallow water-table piezometers, and where the water table is anaerobic (fig. 2).

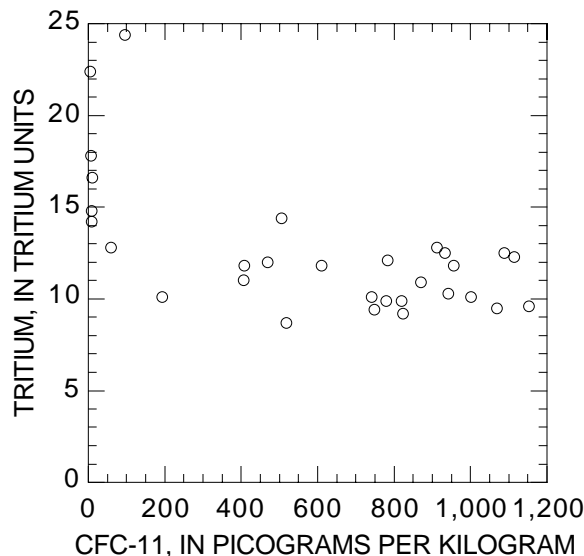


Figure 5. Concentrations of CFC-11 and tritium in water samples from piezometers at the Mirror Lake, New Hampshire, research site.

CFC-113 concentrations in soil gas vary somewhat more than either CFC-12 or CFC-11 concentrations, and several locations exhibit reduced concentrations compared to modern air. The average CFC-113 soil-gas concentration at each sampling location ranged from 0.78 to 1.22 times modern air concentrations. CFC-113 soil-gas concentrations are low near piezometer W33, where zero CFC-113 is measured in shallow water-table piezometers, and where the water table is anaerobic (fig. 2).

CFC concentrations in soil gas show virtually no correlation with depth. In a few cases, however, a systematic pattern in time is present. In these cases, the winter concentrations of soil gas CFC-11 and CFC-113 are a lower fraction of modern air than the summer concentrations. This may be caused by increasing partitioning into the liquid phase as unsaturated zone temperatures decrease. CFC-12 concentrations show no temporal pattern.

DISCUSSION

One of the goals of this field study was to characterize the concentrations of CFC's in

water recharging the saturated zone. Where DO concentrations are relatively high (greater than 5 mg/L), CFC concentrations at the water table appear to be approximately in equilibrium with the modern atmosphere. Even in these well-oxygenated samples, however, CFC concentrations vary widely. The observed range of concentrations in aerobic water-table samples corresponds to uncertainty in ground-water ages determined from CFC-12, CFC-11, and CFC-113 concentrations on the order of ± 4 , 7, and 8 years, respectively. This variability in concentrations at the water table presumably affects the uncertainty in ages associated with water samples from deeper in the saturated zone at the Mirror Lake site. This uncertainty is significantly larger than the analytical uncertainty in the laboratory (± 1 yr).

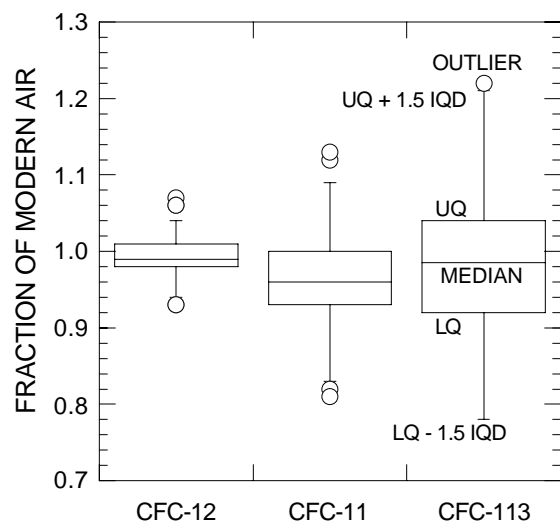


Figure 6. CFC concentrations in soil gas, as a fraction of modern air concentrations, at the Mirror Lake, New Hampshire, research site. (Abbreviations: UQ, upper quartile; LQ, lower quartile; IQD, inner quartile distance = UQ - LQ.)

Samples from piezometers screened near the water table that contain low DO (< 1 mg/L) also contain low CFC's relative to atmospheric equilibrium. In the case of CFC-11 and CFC-113, these compounds are absent from some anaerobic samples. CFC-12 is not reduced as much; concentrations in anaerobic samples are as low as one-third of modern levels. Ground water in the saturated zone that was anaerobic shortly after it was recharged near the water table is likely to have low CFC concentrations. These low CFC concentrations would yield apparent ages for deeper saturated-zone samples

that are much larger than the actual time since recharge.

CFC concentrations are also significantly reduced in samples that have DO concentrations ranging from 1 to 4 mg/L. This pattern is not consistent with degradation of CFC's only under anaerobic conditions because these DO levels are not low enough to be considered anaerobic. This pattern of intermediate CFC concentrations in samples having intermediate DO, however, is consistent with a linear mixing model.

The general pattern of the correlation between CFC's and DO suggests a linear mixing model, although there is scatter in the measurements. This mixing model assumes that samples are linear mixtures of two end-members: (a) aerobic water having about 7 mg/L DO and CFC concentrations in equilibrium with the modern atmosphere; and (b) anaerobic water having no oxygen, no CFC-11 or CFC-113, and CFC-12 concentrations about one-third of modern atmospheric-equilibrium levels. That a water sample pumped from a piezometer with a 0.6- to 0.9-m long screen represents a mixture of water is not surprising. Numerous investigators have reported small-scale variations in ground-water quality. Such small-scale variability is supported by limited diffusion in saturated ground water and by large variations in permeability. Other evidence of mixing of waters is the presence of iron (II) and methane in oxygenated samples. With this mixing model, the lower concentrations in low-DO waters are explained not as degradation under low-DO conditions but as degradation under anaerobic conditions, occurring in only a fraction of the total sample volume.

Although anaerobic degradation of CFC-11 and CFC-113 has been observed in the laboratory (Lovely and Woodward, 1992) and the field (Plummer and others, 1998), CFC-12 degradation has only recently been reported for ground waters (Oster and others, 1996). These field results are consistent with the observations reported herein in that CFC-12 is less degraded, but concentrations of CFC-12 are apparently reduced to as little as one-third of modern levels. This amount of CFC-12 loss would cause tens of years differences between apparent and actual ages of modern ground water.

Independent evidence of anaerobic biodegradation is presented by hydrogen gas, methane, and carbon dioxide concentrations measured in several piezometers (Goode, 1998). Hydrogen-gas concentrations can identify the controlling redox processes in anaerobic systems (Lovely and Goodwin, 1988). Results

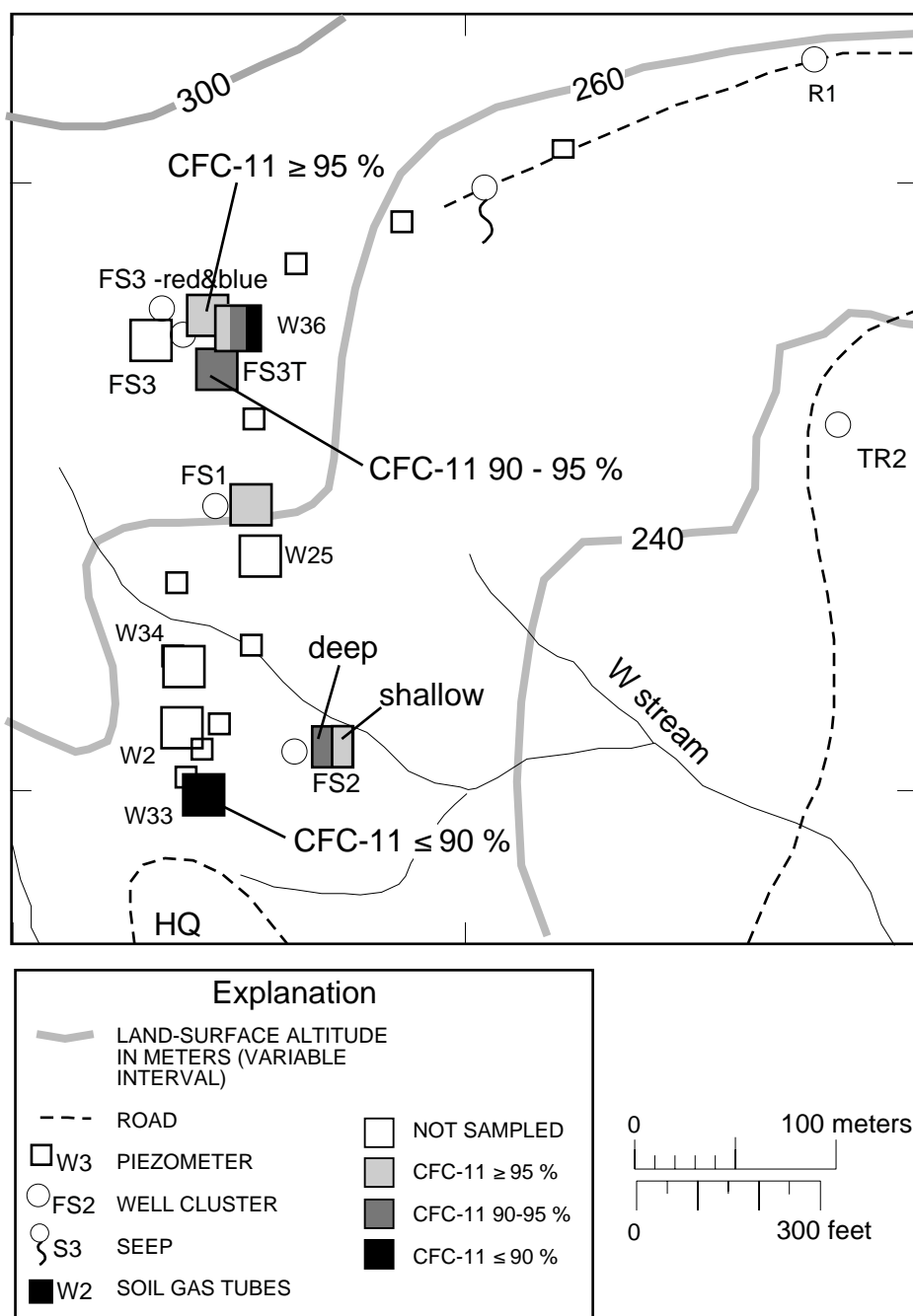


Figure 7. Spatial distribution of CFC-11 concentrations in soil gas, as percentages of modern air concentrations, from sampling tubes at the Mirror Lake, New Hampshire, research site in January 1997.

at anaerobic piezometers indicate methanogenesis is the controlling terminal-electron-accepting-process (TEAP) in piezometer W2, sulfate reduction is the TEAP in W26 and W33, and conditions are intermediate between sulfate reduction and methanogenesis in W25. CFC-11 degradation has been observed in the laboratory for sulfate-reduction and methanogenesis redox conditions (Lovely and Woodward, 1992). Sulfate and iron (II) are present in shallow ground water at Mirror Lake

to support sulfate-reduction and iron-reduction reactions (Goode, 1998). Limited laboratory evidence shows that iron (II) may play a role in abiotic degradation of CFC-11 under anaerobic conditions (Lovely and Woodward, 1992).

Overall, CFC-12 concentrations appear to be least affected by anaerobic degradation or contamination. The use of CFC-12 for age-dating ground water is likely to be more robust in the field, particularly for systems in which anaerobic degradation conditions may exist.

However, even CFC-12 may be degraded to levels that cause tens of years differences in ages.

Given the variability in geochemical conditions observed in different water-table piezometers, it is not possible to characterize the distribution of CFC's in recharge in the Mirror Lake drainage basin on the basis of these 31 piezometers. These results suggest that in areas where the shallow water table is anaerobic, CFC's in recharge will be significantly reduced from modern equilibrium levels. Furthermore, concentrations also may be reduced due to anaerobic degradation in micro-environments, even though the apparent redox conditions in pumped samples are not anaerobic. It is likely, however, that these micro-environments will have relatively low permeability and thus may play a less important role in controlling recharge chemistry, which will be weighted toward conditions in higher-permeability zones.

Although the processes causing anaerobic ground water at the Mirror Lake site have not been fully identified, there appears to be a connection between anaerobic conditions and areas of ground-water/surface-water exchange. A local flow system associated with stream loss and flow across a sandy terrace exhibits strong anaerobic conditions. Shattuck (1991) identified an area in the Mirror Lake drainage basin where the water-table gradient is across the W stream. In this area, stream water may enter the subsurface and flow across the sandy terrace to another branch of the W stream. Concentrations of DO and total organic carbon (TOC) in water-table piezometers located nearly parallel to the apparent flow direction suggest the provision of organic carbon to the aquifer by the stream may contribute to the anaerobic redox conditions (fig. 8). Organic carbon may be carried into the aquifer from the stream bottom. DO is consumed by the biologic activity and is only slowly replenished by diffusion downward through the unsaturated zone. This stream loss is not the only factor contributing to anaerobic conditions, because such low-DO environments also are present upgradient of streams (for example, W25 in fig. 8).

SUMMARY

The use of chlorofluorocarbons (CFC's) as age-dating tracers for ground water at the Mirror Lake fractured-rock research site may be limited because concentrations of CFC's in at least some areas are significantly reduced by anaerobic degradation. CFC concentrations in water samples from high-conductivity fractures

in schist and granite bedrock indicate ages ranging from greater than 45 years to about 7 years, but the spatial pattern of ages is complex and the youngest measured ages are near the lake at the bottom of the forested watershed. Equilibrium between CFC in the atmosphere and at the water table is needed to date saturated-zone waters. Samples from piezometers screened just below the water table in the glacial drift, however, indicate that CFC-11, CFC-12, and CFC-113 are substantially degraded where dissolved oxygen (DO) concentrations are low. Anaerobic ($DO < 0.1$ mg/L) conditions existing in a sandy terrace deposit may be caused by biodegradation of organic carbon in infiltrating stream water. Samples from this and other shallow anaerobic zones lack CFC-11 and CFC-113 and have CFC-12 concentrations as low as one-third of modern equilibrium concentrations. Furthermore, several low-DO ($0.1 < DO < 4$ mg/L) samples have substantially reduced CFC's. As expected, samples with high DO collected at the water table generally contain CFC's near atmospheric-equilibrium concentrations. Many samples plot on a mixing line for CFC's and DO, suggesting that the water sampled can be a mixture of two end members: (1) waters saturated with oxygen and containing CFC's in equilibrium with the

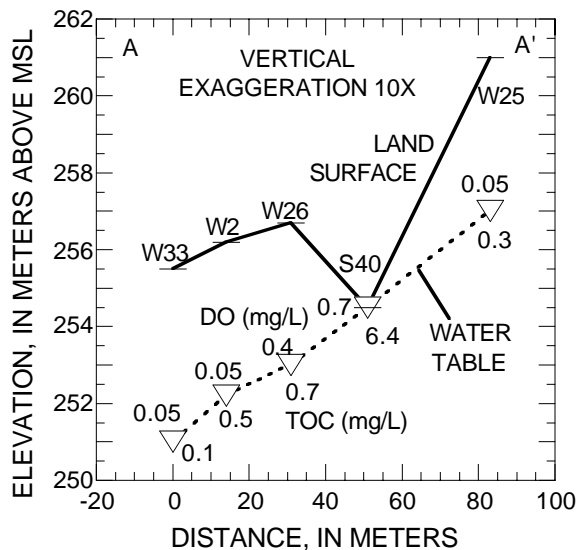


Figure 8. Cross-section A-A' in the lower part of the W stream drainage basin at the Mirror Lake, New Hampshire, research site showing the land surface elevation, water table elevation, and concentrations of dissolved oxygen (DO) and total organic carbon (TOC) in samples from water-table piezometers (indicated by W#). Cross-section location shown in fig. 1. (Abbreviation: MSL, mean sea level)

modern atmosphere, and (2) zero-DO waters containing no CFC-11 or CFC-113 and containing about 1/3 of modern CFC-12. Several samples contain CFC-11 and CFC-113 concentrations higher than those from equilibration with peak atmospheric levels, suggesting a non-atmospheric source. Evidence of active anaerobic biodegradation, which can degrade CFC's, includes high methane, ample iron (Fe-II) and sulfate, and generally low DO. Hydrogen-gas concentrations in anaerobic samples from water-table piezometers are consistent with methanogenesis or sulfate-reduction as the terminal electron-accepting process.

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